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The Use of Slater Orbitals in Variational Calculations Involving One-Electron Green's Functions

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In this paper an application of a minimum principle proposed for electronic systems by Hall, Hyslop and Rees, [1] and [2], is considered. It is shown that the evaluation of the required two-centre molecular integrals involving one-electron Green's functions may be facilitated by the introduction of a particular class of trial functions. These functions incorporate the potential energy of the system as a weighting factor and Slater-type orbitals are then used as a basis set. The evaluation of the resulting integrals is discussed and illustrative calculations for the H_2^+ ion are presented.

Key words: Green's functions – Integrals, molecular

1. Introduction

The variational functional

$$\eta=(\omega V, GV\omega)/(\omega, V\omega) \tag{1}$$

has been considered by Hall and his co-workers, [1] and [2], as an alternative to the normal minimum energy variational principle for atoms and molecules. The functional arises from the conjugate eigenvalue equation, [1], with G being the Green's operator defined by

$$G=(\mu^2 E-T)^{-1} \tag{2}$$

in which E is the energy of the system, T is the electronic kinetic energy operator, and μ is a scaling factor. In Eq.(1), V is the potential energy operator, and $\omega(\boldsymbol{r})$ is an arbitrary trial function.

Details of the scaling techniques used in implementing (1) and also an alternative functional for molecular systems are given in [1] and [2], where applications to the hydrogen atom, and the hydrogen molecular ion H_2^+ have been investigated. It was shown that the method has the advantage of allowing a wider class of trial functions than is possible for the usual minimum energy principle, and also that the energies obtained are always at least as good as those of the Rayleigh-Ritz prescription. The compensating disadvantage is, of course, the increased difficulty of the integrals involved in (1), due to the presence of the Green's operator G.

Attention has been given by Hyslop [3] and by Blakemore, Evans and Hyslop [4] to the evaluation of two-centre molecular integrals involving one-electron

Green's functions. For a certain class of trial functions, techniques have been developed which reduce the order of the numerical integrations by using Fourier transform representations. The resulting triple integrals are then evaluated numerically using improved polar grids for increased efficiency.

In the present paper, a different class of trial functions, which are applicable to two-centre molecular orbital calculations, is considered. The analytical evaluation of the integrals required is treated in some detail, with generalization in mind, and the methods are applied to the hydrogen molecular ion by way of illustration.

2. Separated Atom Trial Functions

In the earlier work [2], [3] and [4] on two-centre integrals, trial functions of the form

$$\omega(\boldsymbol{r})=f(\lambda) \tag{3}$$

are considered, where

$$\lambda=(r_a+r_b)/R \tag{4}$$

r_a and r_b being the distance between the electron and nuclei A and B, whose separation is R. In particular the simple united atom approximation

$$\omega=\exp(-c\lambda) \tag{5}$$

was utilized. Such trial functions are, of course, exact in the united atom limit as $R \to 0$, but give the wrong energies in the separated atom limit as $R \to \infty$. On the other hand, separated atom trial functions of the type discussed by Dalgarno and Poots [5] may well be correct in both limits provided variational parameters such as c in Eq.(5) are incorporated. Such trial functions are written in the form

$$\omega(\boldsymbol{r})=\omega_a(\boldsymbol{r}_a)+\omega_b(\boldsymbol{r}_b) \tag{6}$$

in which the atomic orbitals ω_a and ω_b are centred on nuclei A and B respectively. The functional (1) may be expressed as

$$\eta=I/J \tag{7}$$

where

$$I=G_{aa}+G_{ab}+G_{ba}+G_{bb} \tag{8}$$

and

$$J=V_{aa}+V_{ab}+V_{ba}+V_{bb} \tag{9}$$

with the matrix elements being defined, for example, by

$$G_{ab}=(\omega_a V,\ GV\omega_b) \tag{10}$$

and

$$V_{ab}=(\omega_a,\ V\omega_b) \tag{11}$$

Note that in the case of homonuclear molecules such as H_2^+, symmetry relations such as $G_{aa}=G_{bb}$ and $G_{ba}=G_{ab}^*$ may often be utilised.

It was found that, with this form of trial function, not all of the integrals arising could be reduced analytically to acceptable levels for evaluation. In particular integrals of the "exchange" type

$$(\omega_a r_b^{-1}, G\omega_b r_a^{-1}) \tag{12}$$

presented difficulty.

For this reason, a modification is suggested in which the trial function $\omega(\boldsymbol{r})$ is written

$$V(\boldsymbol{r})\omega(\boldsymbol{r})=\Phi_a(\boldsymbol{r}_a)+\Phi_b(\boldsymbol{r}_b) \tag{13}$$

The integrals (10) and (11) now become

$$G_{ab}=(\Phi_a, G\Phi_b) \tag{14}$$

$$V_{ab}=(\Phi_a, V^{-1}\Phi_b) \tag{15}$$

Trial functions of this form have also been suggested by Schwartz [6] for use in the Schwinger variational principle for scattering problems.

As a simple example, for H_2^+, where

$$V(\boldsymbol{r})=-r_a^{-1}-r_b^{-1} \tag{16}$$

the trial function defined by

$$V\omega=-r_a^{-1}\exp(-cr_a)-r_b^{-1}\exp(-cr_b) \tag{17}$$

could be utilized in a ground state calculation.

It is easily seen that the function is of the correct form as $R \to 0$ and as $R \to \infty$, and also attains the correct hydrogenic form in the vicinity of nucleus A as $r_a \to 0$ and of B as $r_b \to 0$.

More generally, the trial functions used are based on Slater-type orbitals, as in the review paper on the evaluation of molecular integrals by Harris and Michels [7].

Thus in Eq.(13), Φ_a and Φ_b are expressed as linear combinations of the basis set of functions centred on A and B respectively and defined by

$$\phi_a(n, l, m, c)=r_a^{n-2}\exp(-cr_a)\;Y_{l,m}(\theta_a, \phi) \tag{18}$$

$$\phi_b(n, l, m, c)=r_b^{n-2}\exp(-cr_b)\;Y_{l,m}(\theta_b, \phi) \tag{19}$$

with

$$n\geqslant 1, \quad 0\leqslant l\leqslant n-1 \quad \text{and} \quad |m|\leqslant l \tag{20}$$

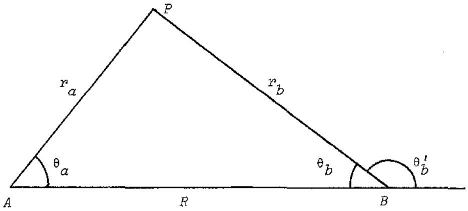

Fig. 1. Polar coordinates

The coordinates used are shown in Fig. 1, ϕ being the azimuthal angle about the axis $\overrightarrow{AB}=\boldsymbol{R}$. The spherical harmonics in Eq. (18) are as defined by Rose [8], and it should be noted that the definition is at variance with that of Harris and Michels (see Appendix).

The functions defined by (18) and (19) are symmetrical with respect to interchange of the nuclei A and B. However, in order to ensure that right-handed reference frames are used at both centres, it is preferable, in some cases, to work in terms of the complementary angle θ'_b shown in Fig. 1.

The orbital ϕ_b is then defined by

$$\phi_b=(-1)^{l+m}r_b^{n-2}\exp(-cr_b)\;Y_{l,m}(\theta'_b,\phi) \tag{19a}$$

3. Evaluation of the Integrals

The matrix elements G_{aa}, G_{ab}, V_{aa} and V_{ab} may be expressed as linear combinations of integrals defined by

$$\begin{aligned} g_{aa}(\boldsymbol{n}_1,\boldsymbol{n}_2)&=(\phi_{a1},G\phi_{a2})\\ g_{ab}(\boldsymbol{n}_1,\boldsymbol{n}_2,R)&=(\phi_{a1},G\phi_{b2})\\ v_{aa}(\boldsymbol{n}_1,\boldsymbol{n}_2,R)&=(\phi_{a1},V^{-1}\phi_{a2})\\ v_{ab}(\boldsymbol{n}_1,\boldsymbol{n}_2,R)&=(\phi_{a1},V^{-1}\phi_{b2}) \end{aligned} \tag{21}$$

In these formulae, the quantum numbers n, l, and m together with the exponent c, which is related to the effective nuclear charge, have been abbreviated according to

$$\boldsymbol{n}=(n,l,m,c) \tag{22}$$

and additional abbreviations, such as ϕ_{ai}, have been used in Eq.(21) to denote

$$\phi_{ai}=\phi_a(\boldsymbol{n}_i)=\phi_a(n_i,l_i,m_i,c_i)\quad i=1,2 \tag{23}$$

3.1. The Integrals v_{aa} and v_{ab}

In the case where Z_a and Z_b are the respective nuclear charges, the potential energy appearing in Eq.(21) is written as

$$V(\boldsymbol{r})=-Z_a/r_a-Z_b/r_b \tag{24}$$

The corresponding integrals are best evaluated using the two-centre elliptic coordinates (λ,μ,ϕ) defined by

$$\lambda=(r_a+r_b)/R,\quad \mu=(r_a-r_b)/R \tag{25}$$

On using definition (A1) in Eqs.(18) and (19) it is at once apparent that the integration over the azimuthal angle ϕ yields the selection rule $m_1=m_2$ in both cases and it is easily demonstrated that v_{aa} and v_{ab} may be written in the forms

$$\begin{aligned} v_{aa}=&-\pi(R/2)^{n_1+n_2}\delta_{m_1,m_2}N_{l_1,m_1}N_{l_2,m_2}\\ &\times\int_1^{\infty}d\lambda\int_{-1}^{+1}\Lambda^{-1}\exp[-\alpha(\lambda+\mu)]\,(\lambda+\mu)^{n_1+n_2-2}(\lambda-\mu)^2\\ &\times P_{l_1}^{m_1}(\cos\theta_a)P_{l_2}^{m_2}(\cos\theta_a)\;d\mu \end{aligned} \tag{26}$$

and

$$v_{ab} = -\pi(R/2)^{n_1+n_2}\delta_{m_1,m_2}N_{l_1,m_1}N_{l_2,m_2}$$
$$\times\int_1^{\infty} d\lambda \int_{-1}^{+1} \Lambda^{-1} \exp[-(\alpha\lambda+\beta\mu)]\,(\lambda+\mu)^{n_1}(\lambda-\mu)^{n_2}$$
$$\times P_{l_1}^{m_1}(\cos\theta_a)P_{l_2}^{m_2}(\cos\theta_b)\,d\mu \tag{27}$$

In these results, the normalization factors are given by Eq.(A2) and α, β and Λ are defined by

$$\begin{aligned}\alpha &= \tfrac{1}{2}R(c_1+c_2)\\ \beta &= \tfrac{1}{2}R(c_1-c_2)\\ \Lambda &= \tfrac{1}{2}(Z_b+Z_a)\lambda+\tfrac{1}{2}(Z_b-Z_a)\mu.\end{aligned} \tag{28}$$

On noting that

$$\cos\theta_a = (1+\lambda\mu)/(\lambda+\mu) \tag{29}$$

and

$$\cos\theta_b = (1-\lambda\mu)/(\lambda-\mu) \tag{30}$$

and utilising definition (A3) for the associated Legendre functions, it is easy to verify that, apart from the Λ^{-1} and exponential factors, the integrands in (26) and (27) are polynomials in λ and μ for all values of the quantum numbers. In fact, the integrals may be expressed in the general forms

$$\int_1^{\infty} d\lambda \int_{-1}^{+1} \Lambda^{-1} \exp(-\alpha\lambda-\alpha\mu)R_{n_1+n_2}(\lambda,\mu)\,d\mu \tag{31}$$

and

$$\int_1^{\infty} d\lambda \int_{-1}^{+1} \Lambda^{-1} \exp(-\alpha\lambda-\beta\mu)S_{n_1+n_2}(\lambda,\mu)\,d\mu \tag{32}$$

where $R_n(\lambda, \mu)$ and $S_n(\lambda, \mu)$ are polynomials in which the highest powers of λ and μ appearing are λ^n and μ^n.

General analytical expressions could be written down for R_n and S_n by expansion. However, it was found to be more expedient to program a computer to perform the required algebraic manipulations directly. The coefficients for the Legendre functions and the binomial expansions are both generated by means of simple recurrence relations. This technique has been frequently adopted in similar instances by Harris and Michels [7].

It is apparent, therefore, that the basic integral required is of the form

$$I_{p,q} = \int_1^{\infty} d\lambda \int_{-1}^{+1} \Lambda^{-1}\lambda^p\mu^q \exp(-\alpha\lambda-\beta\mu)\,d\mu \tag{33}$$

with $0 \leqslant p,\ q \leqslant (n_1+n_2)$ (34)

In the important homonuclear case where the nuclear charge is $Z=Z_a=Z_b$, Λ reduces to $Z\lambda$, and consequently

$$I_{p,q} = Z^{-1}A_{p-1}(\alpha)B_q(\beta) \tag{35}$$

where the standard molecular integrals A_p and B_q are defined by Harris and Michels as

$$\begin{aligned} A_p(\alpha) &= \int_1^\infty \lambda^p \exp(-\alpha\lambda)\, d\lambda \\ B_q(\beta) &= \int_{-1}^{+1} \mu^q \exp(-\beta\mu)\, d\mu \end{aligned} \tag{36}$$

For heteronuclear systems $I_{p,q}$ is obtained by differentiation of the basic result for $I_{0,0}$ defined by

$$I_{0,0} = 2(Z_a+Z_b)^{-1} \int_1^\infty d\lambda \int_{-1}^{+1} (\lambda+\gamma\mu)^{-1} \exp(-\alpha\lambda-\beta\mu)\, d\mu \tag{37}$$

with

$$\gamma = (Z_b - Z_a)/(Z_b + Z_a) \tag{38}$$

It is easily shown that

$$\begin{aligned} I_{0,0} = {} & 2R^{-1}(c_2 Z_b - c_1 Z_a)^{-1} \\ & \times \{\exp(\alpha\gamma-\beta)\, E_1(\alpha+\alpha\gamma) - \exp(\beta-\alpha\gamma)\, E_1(\alpha-\alpha\gamma) \\ & - \exp(\beta\gamma^{-1}-\alpha)[\mathrm{Ei}(-\beta-\beta/\gamma) - \mathrm{Ei}(\beta-\beta/\gamma)]\} \end{aligned} \tag{39}$$

the exponential integrals $E_1(z)$ and $\mathrm{Ei}(z)$ being defined by Abramowitz and Stegun [10].

An alternative approach which has proved convenient in practice is to use the expansion

$$I_{p,q} = 2(Z_a+Z_b)^{-1} \sum_{s=0}^{\infty} (-\gamma)^s A_{p-1-s}(\alpha) B_{q+s}(\beta) \tag{40}$$

Convergence may be speeded up in certain cases by using Euler's transformation or the non-linear transformations of Shanks [11].

3.2. *The Integral* g_{aa}

Taking the origin at nucleus A and introducing the one-electron Green's function

$$g(\boldsymbol{r}_1, \boldsymbol{r}_2) = -(2\pi r_{12})^{-1} \exp(-kr_{12}) \tag{41}$$

corresponding to (2), with $r_{12} = |\boldsymbol{r}_1 - \boldsymbol{r}_2|$ and $\mu^2 E = -\frac{1}{2}k^2$, g_{aa} may be expressed as

$$\begin{aligned} g_{aa}(\boldsymbol{n}_1, \boldsymbol{n}_2) = {} & -\iint f_1(r_1) Y^*_{l_1,m_1}(\theta_1, \phi_1)(2\pi r_{12})^{-1} \exp(-kr_{12}) \\ & \times f_2(r_2) Y_{l_2,m_2}(\theta_2, \phi_2)\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2 \end{aligned} \tag{42}$$

the radial functions appearing in (18) having been abbreviated to

$$f_i(r) = r^{n_i-2} \exp(-c_i r) \qquad (i = 1, 2) \tag{43}$$

Integrals of a similar type have been evaluated by Calais and Löwdin [12], and their method is followed here. Thus, the polar axis of the $\boldsymbol{r}_2$ coordinates is taken along $\boldsymbol{r}_1$, and the new polar angles for $\boldsymbol{r}_2$ are θ_{12} and ϕ_{12}, where θ_{12} is the angle between $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, and ϕ_{12} is the azimuth about the axis $\boldsymbol{r}_1$. This corresponds to a rotation of the old system of co-ordinates through the Euler angles $\alpha=\phi_1$, $\beta=\theta_1$ and $\gamma=0$. The function

$$Y_{l_2,m_2}(\theta_2, \phi_2)$$

is therefore transformed to

$$\sum_{m'} [D^{l_2}_{m_2,m'}(\phi_1, \theta_1, 0)]^* Y_{l_2,m'}(\theta_{12}, \phi_{12}) \tag{44}$$

where the elements of the rotation matrix D are as defined by Rose [8]. Integration over ϕ_{12} shows that $m'=0$ is the only non-vanishing contribution. Hence, noting that

$$D^l_{m,0}(\alpha, \beta, 0)=(4\pi)^{1/2}(2l+1)^{-1/2} Y^*_{l,m}(\beta, \alpha) \tag{45}$$

and completing the angular integrations using the orthonormality properties of the spherical harmonics, it follows that

$$g_{aa}=-\delta_{l_1,l_2}\delta_{m_1,m_2}\int_0^\infty r_1 f(r_1)\,dr_1 \int_0^\infty r_2 f(r_2)\,dr_2$$

$$\times \int_{|r_1-r_2|}^{r_1+r_2} \exp(-r_{12})\, P_{l_2}(\cos\theta_{12})\,dr_{12} \tag{46}$$

with

$$\cos\theta_{12}=(r_1^2+r_2^2-r_{12}^2)/(2r_1r_2) \tag{47}$$

The radial integrations are now possible analytically and may be expressed in terms of the integrals denoted by

$$[klm]=\int_0^\infty r_1^k \exp(-ar_1)\,dr_1 \int_0^\infty r_2^l \exp(-br_2)\,dr_2$$

$$\times \int_{|r_1-r_2|}^{r_1+r_2} r_{12}^m \exp(-cr_{12})\,dr_{12} \tag{48}$$

an analytic form for this integral being presented by Calais and Löwdin. For reference purposes, the result is quoted in a rather more symmetric form as

$$[klm]=2k!\,l!\,m!$$

$$\times \sum_{p=0}^{k}\sum_{q=0}^{l}\sum_{r=0}^{m}\binom{l-q+p}{p}\binom{m-r+q}{q}\binom{k-p+r}{r}$$

$$\times[(a+b)^{l-q+p+1}(b+c)^{m-r+q+1}(a+c)^{k-p+r+1}]^{-1} \tag{49}$$

Once again, the algebraic manipulations required to reduce (46) to the form (48) are best performed on the computer using simple recursion relations for the coefficients.

3.3. The Integral g_{ab}

The basic method employed here is based on the convolution approach summarized by Harris and Michels [7], and subsequently adopted by Blakemore, Evans and Hyslop [4] for united atom Green's function integrals. Thus, on using a Fourier transform representation of the Green's Function $g(\boldsymbol{r}_1, \boldsymbol{r}_2)$, the integral may be written as

$$g_{ab}(\boldsymbol{n}_1, \boldsymbol{n}_2, R) = -(4\pi^3)^{-1} \int \overline{\phi}^{*}_{a1}(s)(s^2+k^2)^{-1}\overline{\phi}_{b2}(s)\, ds \tag{50}$$

where

$$\overline{\phi}_{a1}(s) = \int \phi_{a1}(\boldsymbol{r}) \exp(-i\boldsymbol{s}.\boldsymbol{r})\, d\boldsymbol{r} \tag{51}$$

and

$$\overline{\phi}_{b2}(s) = \int \phi_{b2}(\boldsymbol{r}) \exp(-i\boldsymbol{s}.\boldsymbol{r})\, d\boldsymbol{r} \tag{52}$$

The Fourier transform $\overline{\phi}_{a1}$ may be expressed as

$$\overline{\phi}_{a1} = \exp(-i\boldsymbol{a}.\boldsymbol{s}) \int f_1(r_a) Y_{l_1,m_1}(\theta_a, \phi) \exp(-i\boldsymbol{s}.\boldsymbol{r}_a)\, d\boldsymbol{r}_a \tag{53}$$

The vector $\overrightarrow{AP}$ is denoted by $\boldsymbol{r}_a$, $\boldsymbol{a}$ is the position vector of nucleus A relative to some arbitrary origin, and θ_a and ϕ are the polar co-ordinates of the electron P as shown in Fig. 1. The polar axis is taken along the vector $\boldsymbol{s}$, whose polar co-ordinates relative to the axis $\overrightarrow{AB}$ are (θ_s, ϕ_s), and an angular transformation similar to Eq.(44) is adopted, using Euler angles $\alpha = \phi_s$, $\beta = \theta_s$ and $\gamma = 0$. It is easily verified that

$$\overline{\phi}_{a1} = 4\pi(-i)^{l_1} \exp(-i\boldsymbol{a}.\boldsymbol{s}) Y_{l_1,m_1}(\theta_s, \phi_s) F_1(s) \tag{54}$$

where

$$F_1(s) = (n_1 - 2, l_1, c_1)^T \tag{55}$$

$(n, l, c)^T$ being Geller's notation [13] for the integral

$$(n, l, c)^T = \int_0^\infty r^{n+2} j_l(sr) \exp(-cr)\, dr \tag{56}$$

in which $j_l(z)$ is the spherical Bessel function [10]. A similar result to Eq.(54) is quoted by Harris and Michels. The expression

$$\begin{aligned}(n, l, c)^T = {} & 2^l l!(n-l+1)!c^{n-l+1}s^l(s^2+c^2)^{-n-2} \\ & \times \sum_{\sigma=0}^{\tau} (-1)^\sigma \binom{n+l+2}{2\sigma+2l+1}\binom{\sigma+l}{\sigma} s^{2\sigma}c^{-2\sigma}\end{aligned} \tag{57}$$

with

$$\tau \leqslant \tfrac{1}{2}(n-l+1)$$

has been obtained by Geller [13]. Alternatively, recurrence relations for the generation of $(n, l, c)^T$ are given by Harris and Michels.

In a similar manner, using the right-handed co-ordinate system (19a) in the definition of ϕ_{b2}, it may be shown that

$$\overline{\phi}_{b2} = 4\pi(-1)^{l_2+m_2}(-i)^{l_2} \exp(-i\boldsymbol{b}.\boldsymbol{s})\, Y_{l_2,m_2}(\theta_s, \phi_s) F_2(s) \tag{59}$$

where

$$F_2(s)=(n_2-2,\, l_2,\, c_2)^T \tag{60}$$

The integral g_{ab} may now be written as

$$\begin{aligned} g_{ab}= & -4\pi^{-1}(-1)^{l_2+m_2} i^{l_1-l_2} \\ & \times \int \exp(-i\boldsymbol{R}.\boldsymbol{s})\; Y^*_{l_1,m_1}(\theta_s,\, \phi_s)F_1(s) \\ & \times (s^2+k^2)^{-1}\, Y_{l_2,m_2}(\theta_s,\, \phi_s)F_2(s)\; ds \end{aligned} \tag{61}$$

which represents a generalization of Harris and Michels' result for Coulomb-type integrals.

As in Calais and Löwdin's work, the product of the spherical harmonics is replaced by the Clebsch-Gordon series according to

$$Y^*_{l_1,m_1}(\theta_s,\, \phi_s)Y_{l_2,\,m_2}(\theta_s,\, \phi_s)=\sum_l a_l Y_{l,m}(\theta_s,\, \phi_s) \tag{62}$$

where the coefficients a_l are given by

$$\begin{aligned} a_l= & (-1)^{m_1}[(2l_1+1)(2l_2+1)(4\pi)^{-1}(2l+1)^{-1}]^{1/2} \\ & \times C(l_1,\, l_2,\, l; -m_1,\, m_2,\, m)C(l_1,\, l_2,\, l;\, 0,\, 0,\, 0) \end{aligned} \tag{63}$$

with $|l_1-l_2| \leqslant l \leqslant l_1+l_2$ and $m=-m_1+m_2$, Rose's notation [8] being employed for the Clebsch-Gordon coefficients C. Alternatively a_l may be written in the form

$$\begin{aligned} a_l= & (-1)^{m_2}[(2l_1+1)(2l_2+1)(2l+1)/(4\pi)]^{1/2} \\ & \times \begin{pmatrix} l_1 & l_2 & l \\ -m_1 & m_2 & -m \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} \end{aligned} \tag{64}$$

where the Wigner $3j$-symbols are defined by Edmonds [9], many useful recurrence relations and formulae for their computation being quoted there. Harris and Michels give an alternative expression replacing Eq.(62), which is consistent with the form of atomic orbital which they use.

The angular integrations are now straightforward, and, noting that the azimuthal integral produces the selection rule $m=0$ or $m_1=m_2$, the final result is

$$\begin{aligned} g_{ab}= & -8\pi^{-1/2}\delta_{m_1,m_2} \sum_l i^{l_1-l_2-l}(-1)^{l_2+m_2}(2l+1)^{1/2}a_l \\ & \times \int_0^\infty s^2 j_l(Rs)F_1(s)F_2(s)(s^2+k^2)^{-1}\, ds \end{aligned} \tag{65}$$

The integral appearing in Eq.(65) is again a generalization of the result of Harris and Michels. Analytical treatment of these integrals based on a recurrence relation approach is possible. However, the relations are cumbersome, and have to be modified, for example, when c_1/c_2 approaches unity, due to the presence of removable singularities. These difficulties are typified by the expression for $g_{ab}(1,\, 0,\, 0,\, c_1;\, 1,\, 0,\, 0,\, c_2)$ which is

$$\begin{aligned} g_{ab}= & -8\pi R^{-1}(c_1^2-c_2^2)^{-1}(c_1^2-k^2)^{-1}(c_2^2-k^2)^{-1} \\ & \times \{(c_1^2-c_2^2)\exp(-kR)+(c_2^2-k^2)\exp(-c_1R)-(c_1^2-k^2)\exp(-c_2R)\} \end{aligned} \tag{66}$$

For this reason, numerical evaluation of the integrals was adopted. On writing the spherical Bessel function in the form

$$j_l(z) = u_l(z) \sin z + v_l(z) \cos z \tag{67}$$

(see Abramowitz and Stegun [10], p. 437), the integrand may be split into two components, each with an oscillatory factor of $2\pi/R$. The method of Alaylioglu, Evans and Hyslop [14] was then used to evaluate these components. This consists of integrating over each half-cycle, thus converting the infinite integral into a summation. The convergence of the resulting series is then accelerated using the method of Shanks.

For integration over each half-cycle, the choice of quadrature formula is very wide. In Ref. [14], a low order Gaussian prescription (Stroud and Secrest [15]) was suggested incorporating sub-division of the interval. In practice, it was found that an improvement was obtained by using higher-order Gaussian formulae (maximum order 10).

However the most significant reduction in the total number of function evaluations was produced by employing integration routines specifically designed for oscillatory integrands. Most efficient was a Gaussian prescription based on an oscillatory weight function, but very good results were also obtained by a more flexible method incorporating a Chebyshev fit for the non-oscillatory part of the integrand. In fact, values of the infinite integrals accurate to eight significant figures are obtainable over the complete range of R with a total of about 50 integration points for each value of R.

4. Applications to the H_2^+ Molecule

In general, linear combinations of orbitals Φ_i are employed for the trial function $\omega(\boldsymbol{r})$ according to

$$V\omega = \sum_{i=1}^{N} \gamma_i \Phi_i \tag{68}$$

where, in the notation of Eqs. (18)–(23),

$$\Phi_i = \phi_{ai} + \phi_{bi} = \phi_a(n_i, l_i, m_i, c_i) + \phi_b(n_i, l_i, m_i, c_i) \tag{69}$$

Eq. (68) is generalized in the case of hetero-nuclear diatomic molecules by replacing $\gamma_i \Phi_i$ by

$$\gamma_{ai} \phi_a(n_i, l_i, m_i, c_{ai}) + \gamma_{bi} \phi_b(n_i, l_i, m_i, c_{bi}) \tag{70}$$

where $\gamma_{ai}, \gamma_{bi}, c_{ai}, c_{bi}$ are, in general, treated as independent variational parameters. The correct behaviour in all limits is still obtained if the condition

$$c_{ai}/c_{bi} = Z_a/Z_b \tag{71}$$

is imposed, hence reducing the number of independent variational parameters.

As in the previous work [1]–[4], it is convenient to work in terms of the scaled variables $\boldsymbol{x}$ where

$$\boldsymbol{x} = k\boldsymbol{r} \tag{72}$$

so that trial functions of the form

$$\omega(kr) \tag{73}$$

are employed. This means that the Green's operator becomes

$$G=(-\tfrac{1}{2}-T)^{-1} \tag{74}$$

and has associated Green's function

$$g(\boldsymbol{x}_1, \boldsymbol{x}_2)=-(2\pi x_{12})^{-1}\exp(-x_{12}) \tag{75}$$

where $x_{12}=|\boldsymbol{x}_1-\boldsymbol{x}_2|$, all distances being multiplied by the scaling factor k. In particular, the scaled internuclear separation is denoted by

$$P=kR \tag{76}$$

Functional (1) may then be written as

$$k=(\omega V, GV\omega)/(\omega, V\omega) \tag{77}$$

and minimization of the energy $E=-\frac{1}{2}k^2$ with respect to the parameters γ_i produces the secular equation

$$|G_{ij}-kV_{ij}|=0 \tag{78}$$

where the matrix elements are given by

$$G_{ij}=(\Phi_i, G\Phi_j)=(\phi_{ai}+\phi_{bi}|G|\phi_{aj}+\phi_{bj}) \tag{79}$$

$$V_{ij}=(\Phi_i, V^{-1}\Phi_j)=(\phi_{ai}+\phi_{bi}|V^{-1}|\phi_{aj}+\phi_{bj}) \tag{80}$$

the integrals involved being of the forms specified in Eq.(21).

The approximate energy $E=-\frac{1}{2}k^2$ is now obtained from (78) by selecting the largest root for the ground state. Further optimization over the non-linear parameters c_i appearing in the orbitals Φ_i is now carried out using the method of Powell [16] (N.A.G. routine E04CAF).

By way of illustration, the following combinations of atomic orbitals were considered as trial wavefunctions, and approximate ground state energies computed in each case:

$$\begin{aligned}
&(I) && V\omega=\Phi(1,0,0,c)\\
&(II) && V\omega=\gamma_1\Phi(1,0,0,c)+\gamma_2\Phi(2,0,0,c)\\
&(III) && V\omega=\gamma_1\Phi(1,0,0,c_1)+\gamma_2\Phi(2,1,0,c_2)\\
&(IV) && V\omega=\gamma_1\Phi(1,0,0,c_1)+\gamma_2\Phi(2,0,0,c_1)+\gamma_3\Phi(2,1,0,c_2)\\
&(V) && V\omega=\gamma_1\Phi(1,0,0,c)+\gamma_2\Phi(2,0,0,c)\\
& && \quad+\gamma_3\Phi(2,1,0,c)+\gamma_4\Phi(3,0,0,c)\\
& && \quad+\gamma_5\Phi(3,1,0,c)+\gamma_6\Phi(3,2,0,c)
\end{aligned} \tag{81}$$

The results obtained are presented in Table 1 where values of the electronic energy are shown at various scaled internuclear separations for the five trial functions. The exact energies were obtained by interpolation from the results of

Table 1. Electronic energies, $-E=\frac{1}{2}k^2$, at scaled internuclear distances, $P=kR$

P	(*I*)	(*II*)	(*III*)	(*IV*)	(*V*)	Exact
0.5	1.8907	1.8915	1.8924	1.8937	1.8937	1.8943
1.0	1.6912	1.6976	1.7025	1.7079	1.7079	1.7086
1.5	1.4896	1.5032	1.5129	1.5217	1.5219	1.5224
2.0	1.3135	1.3303	1.3452	1.3553	1.3560	1.3564
2.5	1.1684	1.1841	1.2032	1.2130	1.2144	1.2147
3.0	1.0517	1.0642	1.0853	1.0937	1.0959	1.0961
3.5	0.9587	0.9675	0.9886	0.9951	0.9979	0.9982
5.0	0.7801	0.7819	0.7958	0.7975	0.8002	0.8004
7.0	0.6725	0.6726	0.6771	0.6772	0.6781	0.6783
10.0	0.6109	0.6109	0.6117	0.6117	0.6118	0.6118

Table 2. Equilibrium values for H_2^+

	(*I*)	(*II*)	(*III*)	(*IV*)	(*V*)	Exact
R_0	2.080	2.002	2.018	1.985	1.998	2.000
W_0	0.5683	0.5780	0.5942	0.6008	0.6024	0.6026

Wind [17]. Also in Table 2 the equilibrium internuclear distances, R_0, are presented together with the corresponding minimum total energies

$$W_0=E(R_0)+1/R_0 \tag{82}$$

These equilibrium values are obtained as in Ref. [2] by optimizing

$$W(P)=-\tfrac{1}{2}k^2(P)+k(P)/P \tag{83}$$

with respect to P.

Trial functions (*I*) and (*II*) suffer from the defect that the V^{-1} term gives relatively too little weight to the region between the nuclei, and both give somewhat disappointing energies, though the results given by (*II*) may be improved slightly by employing separately varying exponents. The defect may be remedied by introducing polarization terms with $l=1$ as shown in (*III*) and (*IV*), (see also Dalgarno and Poots [5]), where further flexibility is obtained by using independently varying exponents in the additional terms.

However, if only one independent variational parameter is used in the exponents, the required two-dimensional optimization is reduced to a one-dimensional optimization. The resulting savings in computer time are most usefully employed by incorporating a larger basis set of atomic orbitals. This idea prompted the use of trial function (*V*), which, although requiring, in total, no more integral evaluations than (*IV*), gave much better energies. A further calculation was performed using the same basis set as in (*V*), except that the exponent of each atomic orbital was constrained according to

$$c_i/c_j=n_i/n_j \tag{84}$$

as in the calculations of Nesbet and Watson [18] on atomic Helium. This attempts to localize the orbitals with larger principal quantum number, but no further improvement in the energies was obtained.

In fact, it appears in general that, for a given number of orbitals, the approximate energy values are not particularly sensitive to the choice of the parameters c_i. Hence, no great improvement is realized by independent variation of these parameters, although a considerable increase in computational effort is required. The alternative procedure of extending the basis set to include extra orbitals appears to be preferable, and results in rapid improvement in the approximate energy levels.

Appendix. Definition of the Spherical Harmonics $Y_{l,m}(\theta, \phi)$

The definition adopted is the commonly accepted one presented by Edmonds [9] and by Rose [8], namely,

$$Y_{l,m}(\theta, \phi) = (-1)^m N_{l,m} P_l^m(\cos\theta) \exp(im\phi) \tag{A1}$$

where the normalization constant is given by

$$N_{l,m} = [(2l+1)(l-m)!]^{1/2}/[4\pi(l+m)!]^{1/2} \tag{A2}$$

The associated Legendre functions are defined by

$$P_l^m(x) = (1-x^2)^{m/2} D^{m+l}(x^2-1)^l/(2^l l!) \tag{A3}$$

with $D = d/dx$ and $x = \cos\theta$.

It will be noted that these definitions are applicable for both positive and negative values of m and imply that

$$P_l^{-m}(x) = (-1)^m \frac{(l-m)!}{(l+m)!} P_l^m(x) \tag{A4}$$

and consequently produce the symmetry relation

$$Y_{l,m}^*(\theta, \phi) = (-1)^m Y_{l,-m}(\theta, \phi) \tag{A5}$$

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